



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|---|--|--|---|
| (51) International Patent Classification 6 : D21H 17/52, C08G 59/14 | | A1 | (11) International Publication Number: WO 99/67463 (43) International Publication Date: 29 December 1999 (29.12.99) |
| (21) International Application Number: PCT/IB99/01155 (22) International Filing Date: 21 June 1999 (21.06.99) | | (81) Designated States: AU, BR, CA, CN, JP, NO, US, ZA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). | |
| (30) Priority Data: 9813246.7 22 June 1998 (22.06.98) GB | | Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> | |
| (71) Applicant (<i>for all designated States except JP US</i>): CLARIANT FINANCE (BVI) LIMITED [--]; Citco Building, Wickhams Cay, P.O. Box 662, Road Town, Tortola (VG). | | | |
| (71) Applicant (<i>for JP only</i>): CLARIANT INTERNATIONAL LTD. [CH/CH]; Rothausstrasse 61, CH-4132 Muttenz (CH). | | | |
| (72) Inventor; and (75) Inventor/Applicant (<i>for US only</i>): FARRAR, John, F. [GB/GB]; 47 Layton Lane, Rawdon, Leeds LS19 6RQ (GB). | | | |
| (74) Agents: D'HAEMER, Jan et al.; Clariant International Ltd., Rothausstrasse 61, CH-4132 Muttenz (CH). | | | |

(54) Title: POLYCATIONIC POLYMERS, THEIR PRODUCTION AND USE

(57) Abstract

Polycationic polyquaternary products are obtainable by reaction of an oligohydroxyalkane with epichlorohydrin to a chloroterminated adduct and quaternizing, optionally cross-linking the adduct with at least one aliphatic mono- or oligoamine. The products are useful as adjuvants in paper-making, especially as fixatives in the production of paper from coated broke.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|---------------------------------------|----|---|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakhstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |
| EE | Estonia | | | | | | |

POLYCATIONIC POLYMERS, THEIR PRODUCTION AND USE

In the production of paper from aqueous papermaking furnish (stock) - depending on the various employed materials, i.e. pulps (pulps from virgin fibre, broke and/or reclaimed paper) and wet end additives, equipment and process conditions - the stock may contain a certain amount of dissolved components and suspended very fine to microscopic size components, which will normally not be retained completely in the paper web, but will be present in the white water, in which the suspended particles are visible as turbidity.

In the preparation of stock for papermaking the following operations are usually involved: 1) pulping, 2) beating and refining, 3) addition of wet end chemicals and 4) metering and blending.

In 1) [pulping] the various fibrous materials (virgin fibre, broke, reclaimed papers) are dispersed in water by means of suitable dispersing devices (pulpers, deflakers).

By 2) [beating or refining] the fibres are physically modified (by removing of primary fibre wall, bruising, swelling, hydration, etc....) in such a way as to be suitable for the desired paper production.

Operations 1) and 2) may, if desired, be combined with each other.

Before conveying the stock to the papermaking machine of the assembly, any wet end chemicals are admixed [operation 3)].

If desired, before addition of 3), different kinds of papermaking materials are metered and blended [operation 4)]. Machine broke or reclaimed paper (the latter is suitably also deinked) are preferably repulped separately and then metered and blended with another pulp.

A paper furnish stock often contains pre-refined virgin fibres blended with broke, or for recycled paper, deinked reclaimed fibres optionally blended with broke.

The various components of the white water resulting from drainage, may derive mainly from the following stages: from stages 1) and/or 2) there may result e.g. lignin sulphonates, lignin degradation

CONFIRMATION COPY

products, wood extractives, cellulose derivatives (e.g. hemicellulose). From stages 3) and 4) and in particular from the use of optionally coated broke or reclaimed paper there may result components derived from fillers (e.g. white pigments, dispersants, wetting agents, etc....), from other additives (e.g. modified starches, carboxymethylcellulose, sizing agents, dispersants, dyes, fluorescent whitening agents, coating binders, wetting agents, sodium silicates, biocides, deinking soaps, etc....) and from the employed water (e.g. humic acids and water hardness salts).

The kind and proportion of such contaminants (dissolved components and fine to microscopic suspended components) in the backwater may vary broadly. Their amounts are particularly relevant in stocks from broke or reclaimed paper and where white water is recycled in the system. These backwater components represent an encumbrance of the backwater in particular with a view to its purification, and furthermore – especially where white water is recycled in the system – the presence of the above mostly anionic contaminants may lead to production problems, e.g. to sheet breaks or loss of sheet quality (e.g. holes and non-uniformity), and may impair the activity of cationic additives (such as flocculants, drainage assistants, retention aids, wet strength resins, synthetic sizing agents, cationic dyes, etc....) by forming inactive complexes with the anionic contaminants.

It is thus desirable to find a means for reducing the quantity of such backwater components and for enhancing the activity of any cationic wet end additives. In EP-A 0810322 there are described certain polyaminoethers, obtained by reaction of polyethyleneglycol, epichlorohydrin and certain primary diamines with alkaline crosslinking, which are indicated in the specification as being suitable as retention and drainage agents, fixatives and flocculants; the problem to which the there described invention refers however only in the retention and drainage efficiency in paper production and an improvement over the state of the art is mentioned only in relation to drainage and retention.

From EP-A-810322, WO-A-95/15996, US-A-4056510 and US-A-4281199 there are known certain polymers from reaction products of polyol/epichlorohydrin adducts with polyamines, which are essentially non-quaternary, and may be used in various phases of paper production, also as additives to the pulp.

It has now surprisingly been found that the below defined polycationic, polyquaternary polymers (P) of high cationic density are of outstanding efficiency in particular as fixatives in the production of paper.

The invention relates to the polycationic polymers (P) defined below, their production and use, and aqueous compositions thereof.

The invention thus provides a polycationic polyquaternary product (P) obtainable by reaction of

- (A) an oligohydroxyalkane of molecular weight ≥ 92 , in which the the alkane backbone is optionally interrupted by one or more ether bridges,
or a mixture of two or more thereof,
or a mixture one or more thereof with a C₂₋₃-alkanediol,

with (B) epichlorohydrin,

in the ratio of at least 1 mole of epichlorohydrin for every moleequivalent of oligohydroxycompound of molecular weight ≥ 92 plus 1-4 moles of epichlorohydrin for every moleequivalent of C₂₋₃-alkanediol, to give a chloro-terminated adduct (E),

and quaternizing, optionally cross-linking, reaction of (E) with

- (C) at least one aliphatic mono or oligoamine containing on average not more than one nitrogen-bound hydrogen per nitrogen atom.

As oligohydroxyalkanes of molecular weight ≥ 92 there may be employed known compounds, in particular low molecular oligohydroxyalkanes with 3 to 6 hydroxy groups or polyalkyleneglycols. Preferably (A) is selected from

- (A₁) an oligohydroxyalkane of the formula



in which

- X signifies the x₁-valent radical of a C₃₋₆-alkane
and x₁ signifies a number from 3 to the number of carbon atoms in X,
or a mixture of oligohydroxyalkanes of formula (Ia),
or a mixture one or more oligohydroxyalkanes of formula (Ia) with a C₂₋₃-alkanediol,

and (A₂) a polyalkylene glycol of the average formula



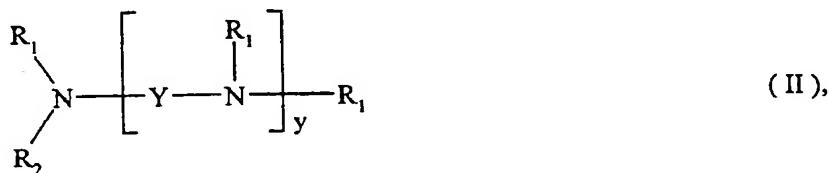
wherein

Alkylene signifies C₂₋₄-alkylene

and x2 signifies a number from 2 to 40.

As amines (C) there may be employed known aliphatic mono- or oligoamines in which at least some of the amino nitrogens are substituted with an aliphatic substituent that does not interfere with the reaction, preferably low molecular alkyl or hydroxyalkyl. (C) is preferably selected from

(C₁) at least one aminocompound of formula



wherein

Y signifies C₂₋₃-alkylene,

y signifies a number from 0 to 3,

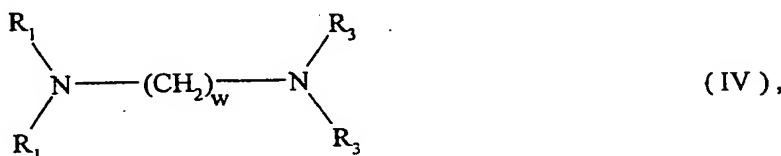
R₁ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl

and R₂ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl, if y is 1 to 4,
or hydrogen, if y is 0,

(C₂) a tertiary amine of formula



and (C₃) at least one diamine of formula



wherein R_3 signifies hydrogen, C_{1-3} -alkyl or C_{2-3} -hydroxyalkyl
and w signifies a number from 2 to 6.

The process for the production of (P) is thus characterized in that (A) is reacted with (B) in the above indicated ratio of (B) to (A), to give a chloro-terminated adduct (E), and (E) is reacted with (C) to give a polyquaternary product.

The reaction components and their molar ratios are chosen so that a polyquaternary product, i.e. a product with at least two quaternary ammonium groups per molecule, is formed, preferably so that a product of polymeric character is formed, i.e. a product that contains repeating units derived from (A), in particular cross-linked products, or/and in which (A) is of polymeric character in particular a polyalkyleneglycol preferably corresponding to (A₂).

According to a preferred feature the invention thus provides polycationic, polyquaternary polymers (P₁) obtainable by reaction of

(A₁) an oligohydroxyalkane of the formula



in which

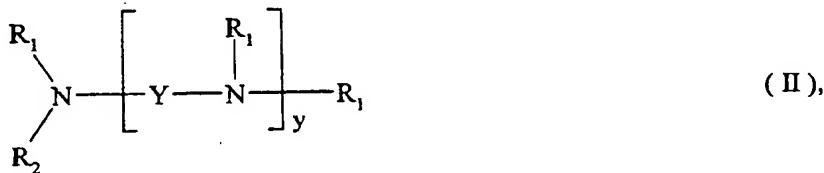
X signifies the x-valent radical of a C_{3-6} -alkane
and $x1$ signifies a number from 3 to the number of carbon atoms in X,
or a mixture of oligohydroxyalkanes of formula (Ia),
or a mixture one or more oligohydroxyalkanes of formula (Ia) with a C_{2-3} -alkanediol,

with (B) epichlorohydrin

in the ratio of (2 to 2x) moles of epichlorohydrin for every mole of compound of formula (Ia) plus 1-4 moles of epichlorohydrin for every mole equivalent of C_{2-3} -alkanediol, to give a chloro-terminated adduct (E₁),

and reaction of (E₁) by cross-linking, quaternizing reaction with

(C₁) at least one aminocompound of formula



in which

- Y signifies C₂₋₃-alkylene,
- y signifies a number from 0 to 3,
- R₁ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl
- and R₂ has a significance of R₁, if y is 1 to 3,
or signifies hydrogen, if y is 0,

and optionally chain-terminating, quaternizing reaction with

(C₂) a tertiary amine of formula



The process for the production of (P₁) is thus characterized in that (A₁) is reacted with (B) in the ratio of (2 to 2x) moles of (B) for every mole of compound of formula (Ia) – plus 1-4 moles of (B) for every moleequivalent of C₂₋₃-alkanediol, to give a chloro-terminated adduct (E₁), and (E₁) is reacted with (C₁) and optionally (C₂).

As oligohydroxyalkanes of formula (Ia) there may be employed known compounds, e.g. glycerol, threitol, trimethylol-ethane or -propane and reduction products of conventional carbohydrates with five or six carbon atoms, such as sorbitol, mannitol, dulcitol and pentaerythritol.

Preferred compounds of formula (Ia) are those of formula



The compounds of formula (Ia) with four to six carbon atoms may be employed in the form of racemic mixtures or of single optical isomers; they are solid at ambient temperature and are thus expediently

employed in admixture with at least one compound selected from glycerol, ethylene glycol and propylene glycol, which are liquid at ambient temperature. The quantitative ratio of such mixtures is chosen suitably so that the mixture is liquid at the chosen reaction temperature; preferably in the range of 1 to 4 parts by weight of compound of formula (Ia) with four to six carbon atoms for every part by weight of compound with two to three carbon atoms. Most preferably there is employed a mixture of a compound of formula (Ia') in which x_1 is 5 or 6, with the compound of formula (Ia') in which x_1 is 3 (i.e. glycerol).

The molar ratio of epichlorohydrin (B) to oligohydroxycompound or mixture (A₁) is preferably in the range of 3 to $1.5 \cdot x_1$ moles, 3 to x_1 moles, of epichlorohydrin per mole of compound of formula (Ia) plus 1-4 moles, preferably 1-2 moles of epichlorohydrin per mole equivalent of C₂₋₃-alkanediol.

According to another preferred feature the invention provides polycationic, polyquaternary products (P₂) obtainable by reaction of

(A₂) an oligoalkylene glycol of the average formula



wherein

Alkylene signifies C₂₋₄-alkylene

and x₂ signifies a number from 2 to 40.

with (B) epichlorohydrin,

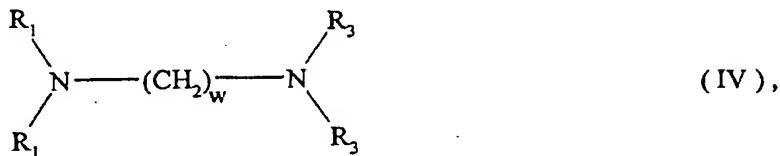
in the ratio of 2 or more, preferably 2 to 8, moles of epichlorohydrin for every mole of oligoalkylene glycol, to give a chloro-terminated adduct (E₂),

and reaction of (E₂) with

(C₂) a tertiary amine of formula



or (C₃) at least one diamine of formula



wherein R_3 signifies hydrogen or C_{1-3} -alkyl
and w signifies a number from 2 to 6.

The process for the production of (P_2) is thus characterized in that (A_2) is reacted with (B) in the ratio of 2 moles of (B) for every mole of diol of formula (Ib) to give a chloro-terminated adduct (E_2), and (E_2) is reacted with (C_2) or (C_3).

Alkylene in formula (Ib) is ethylene, propylene and/or butylene and the polyalkyleneglycols of formula (Ib) may be homo- or copolymers, preferably water soluble products (with a solubility in water of at least 10 g/l at 20°C and pH 7). As polyalkyleneglycols of formula (Ib) there are preferably employed polyethyleneglycols or copolyalkyleneglycols containing a prevailing molar proportion of ethyleneoxy-units. More preferably there are employed polyethyleneglycols, i.e. compounds of formula (Ib) in which Alkylene signifies only ethylene.

For the reaction of (E_2) with (C_2) to give preferably diquaternary products (P_2') are preferred higher molecular weight starting polyethylene glycols (A_2), in particular those in which x_2 is in the range of 4 to 40 more preferably 5 to 36, while for the reaction of (E_2) with (C_3) to give polyquaternary products (P_2'') are preferred lower molecular weight starting polyethylene glycols (A_2), in particular those in which x_2 is in the range of 2 to 24 more preferably 3 to 12.

The reaction of (A) with (B) is preferably carried out in the absence of any other solvent and in the presence of a catalyst, which is e.g. a Lewis acid preferably boron trifluoride preferably in the form of its etherate or acetic acid complex. This reaction is an addition reaction of the epichlorohydrin to a hydroxy group, with opening of the epoxy ring and formation of a 2-hydroxy-3-chloropropyl-1 radical. This reaction is exothermic and the reaction temperature is preferably kept below 100°C, more preferably in the range of 60 to 85°C, with cooling. The epichlorohydrin reacts with the available hydroxy groups of (A) and, as reaction proceeds, may also react with a hydroxy group of a 2-hydroxy-3-chloropropyl-1 radical formed during the reaction, so that some of the hydroxy groups of formula (I) may even remain non-reacted with (B). Depending on the molar ratio, on the functionality of the oligohydroxycompound (e.g. the value of x_1) and on the optical configuration of formula (Ia) -

especially if x_1 is 4 to 6 - the degree of reaction of the OH groups of (A) with (B) may vary, and may e.g. be in the range of 50 to 95 % of the total number of OH groups originally present in (A). The obtained adduct (E) is a chloro-terminated product. This is then reacted with (C).

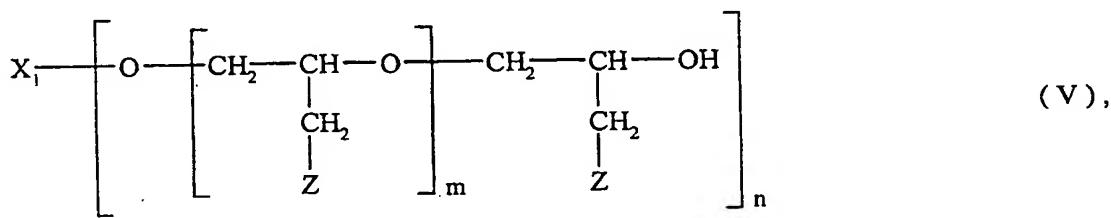
The $C_{1,3}$ -alkyl radicals in R_1 , R_2 and R_3 may be methyl, ethyl, propyl or isopropyl, the lower molecular ones being preferred, especially ethyl and methyl. The $C_{2,3}$ -hydroxyalkyl radicals are preferably 2-hydroxyethyl or -propyl. Among the $C_{1,3}$ -alkyl radicals and the $C_{2,3}$ -hydroxyalkyl radicals the $C_{1,3}$ -alkyl radicals are preferred, especially ethyl or methyl. The index y in formula (II) may be any number from 0 to 3 preferably 0 to 2, more preferably 0 or 1. Representative amines of formula (II) are dimethylamine, diethanolamine, tetramethylethylenediamine, tetramethylpropylenediamine, N,N-diethanol-N',N'-dimethylethylenediamine, pentamethyldiethylenetriamine and hexamethyltriethylenetetramine, among which the difunctional amines, in particular the lower molecular ones, are preferred, especially dimethylamine and tetramethylethylenediamine. Representative amines of formula (III) are trimethylamine, triethylamine and triethanolamine, among which trimethylamine and triethylamine are preferred. In formula (IV) the index w preferably is 2 or 3. Representative amines of formula (IV) are N,N-dimethylaminopropylamine, N,N-diethanolaminopropylamine, tetramethylethylenediamine, tetramethylpropylenediamine and N,N-diethanol-N',N'-dimethylethylenediamine.

The molar ratio of (C) to (E) is preferably chosen so that a product (P) with a density of quaternary ammonium groups as high as possible and preferably polymeric character is produced. The molar ratio of (C_1) to (E_1) is preferably chosen so that for every mole-equivalent of (E_1) referred to chlorine there is employed 0.5 mole of (C_1) \pm 30 %, e.g. \pm 10 %. The molar ratio of (C_2) to (E_2) is preferably chosen so that for every mole-equivalent of (E_1) referred to chlorine there is employed 1 mole of (C_2) \pm 30 %, e.g. \pm 10 %. The molar ratio of (C_3) to (E_2) is preferably chosen so that for every mole-equivalent of (E_2) referred to chlorine there is employed 0.9 mole of (C_3) \pm 40 %, e.g. \pm 20 % (if both R_3 are hydrogen) or 0.5 mole of (C_3) \pm 30 %, e.g. \pm 10 % (if both R_3 are other than hydrogen) or 0.7 mole of (C_3) \pm 35 %, e.g. \pm 15 % (if one R_3 is hydrogen and the other is other than hydrogen).

The reaction of (C) with (E) is carried out suitably in aqueous medium, e.g. at a water content in the range of 20 to 90 %, preferably 30 to 80 %, referred to the total weight of the aqueous reaction mixture, and preferably with heating, e.g. at a temperature in the range of 50 to 100°C, preferably 60 to 95°C. During the reaction, at least at the beginning, the basicity of the amine (C) is sufficient for the quaternizing alkylation of (C) with the chloride (E) used as an alkylating agent. The pH of the reaction mixture is preferably in the range of 4 to 9, at the beginning being preferably in the range of 7 to 9. As reaction proceeds, the alkalinity of the mixture and the concentration of (C) diminish. If in the reaction

product there is present a proportion of covalently linked chlorine which is higher than desired, there may e.g. be added a further reactant which is a compound (C_2) and/or a suitable strong base, such as an alkali metal hydroxide, preferably sodium hydroxide; if the starting crosslinking reactant is a secondary monoamine [e.g. if in formula (II) y is zero], a suitable strong base, such as an alkali metal hydroxide, preferably sodium hydroxide, is expediently added for promoting quaternization, the pH being preferably maintained in the range of 7 to 9. When the reaction has completed or has reached the desired degree, the reaction mixture is suitably acidified by addition of a conventional acid, preferably a mineral acid (such as hydrochloric acid, sulphuric acid or phosphoric acid) or a low molecular aliphatic carboxylic acid e.g. with 1 to 6 carbon atoms (such as formic acid, acetic acid, citric acid or lactic acid), preferably to reach a pH below 6, more preferably in the range of 3 to 5. The proceeding of the reaction may be pursued by checking the viscosity of the reaction mixture, which gives an empirical impression of the degree of crosslinking, i.e. quaternization. A suitable viscosity is e.g. ≤ 5000 cP, preferably in the range of 200 to 3000 cP.

The obtained polymers (P_1) may schematically be represented, at least for the derivatives of compounds of formula (Ia), by the following average formula:



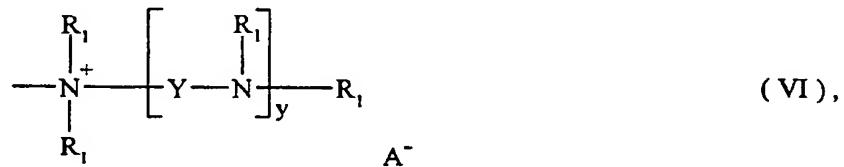
wherein

- X_1 signifies the n -valent radical of an oligohydroxyalkane (A_1) of formula (Ia) as defined above,
- n signifies a number from 2 to x ,
- m signifies a number from 0 to 3
- and Z signifies the quaternary ammonium radical derived from (C_1) or respectively (C_3), or if y signifies 0 may also signify a corresponding tertiary amine radical, and/or two or more symbols Z of a same molecule or of two or more different molecules form together a mono-, bis-, tris or tetra-quaternary bridge derived from the cross-linking reaction of (C_1),

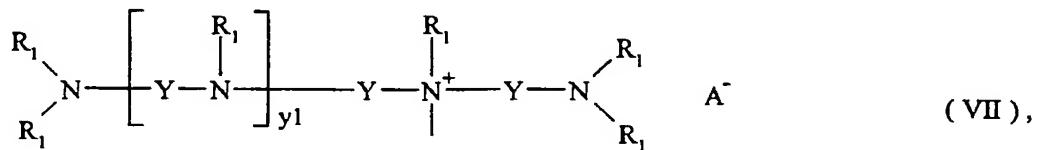
with the proviso that formula (IV) contains at least one quaternary ammonium group.

More particularly the radicals Z containing the quaternary ammonium group may be represented by the following formulae:

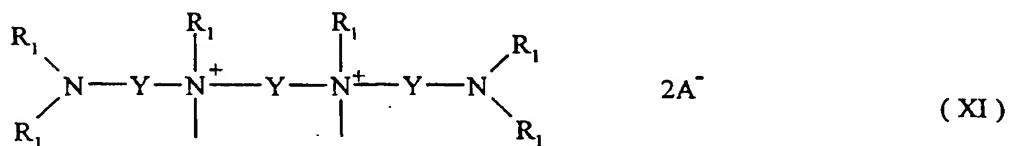
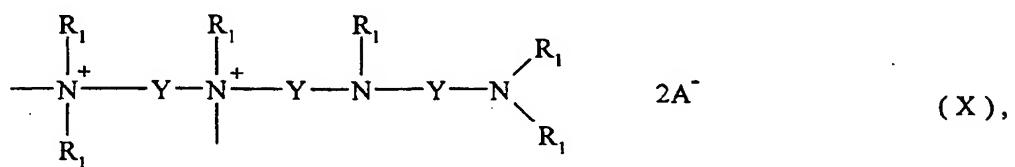
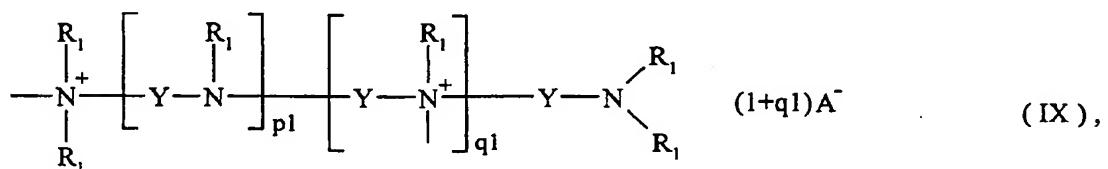
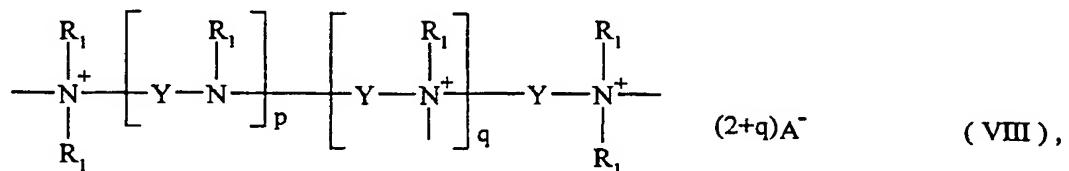
monovalent quaternary radicals Z of formula



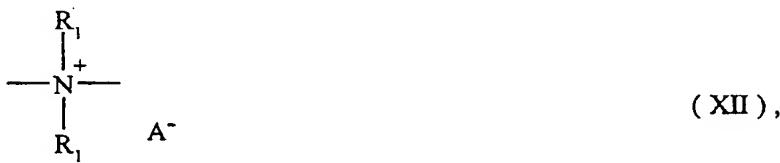
or



and cross-linking bridges, formed by two or more substituents Z together, of formula



or



in which A^- signifies an anion,

y_1 signifies 0 or 1,

p signifies 0 to 2,

q signifies 0 to 2,

p_1 signifies 0 to 1,

q_1 signifies 1 to 2,

$p + q$ is 0 to 2

and $p_1 + q_1$ is 1 to 2.

In formula (V) the index n may have a value lower than x , especially where x is in the range of 4 to 6. n is e.g. in the range of 2 to 4. In formula (VIII) q is preferably 0 and in formula (IX) the index q_1 preferably signifies 1.

In the above formula the counter-ion A^- may be any anion formed during quaternization or by subsequent acidification, preferably chloride or formate.

Among the above products (P) the cross-linked ones are preferred.

The so produced compositions are ready for use or may, if desired, be adjusted in (P) content by dilution with water or evaporation or be desalinated and optionally concentrated by membrane filtration through a semipermeable membrane.

The concentration of (P) in the aqueous composition as produced is preferably in the range of 10 to 80 % by weight, more preferably 20 to 70 % by weight.

The so produced polymers (P), expediently in the form of aqueous composition as produced by the method described above, serve as assistants in the production of paper, in particular as fixatives, for

reducing the amount of backwater components, e.g. turbidity, in backwaters (white waters) from paper production.

The invention thus provides also a method for producing paper, in particular a paper web or sheet, from aqueous stock, wherein (P) is employed as an adjuvant, especially as a fixative. As "paper" there is intended herein also paper board and cast paper shapes. As an aqueous stock there is intended any stock, in particular cellulosic stock, as employed for papermaking and wherein the pulp suspension may derive from any origin as conventionally employed for papermaking, e.g. virgin fibre (chemical or mechanical pulp), machine broke (in particular coated broke) and reclaimed paper (especially deinked and optionally bleached reclaimed paper). The aqueous paper pulp or stock may also contain further additions as may be desired for a certain quality, such as sizing agents, dyestuffs, optical brighteners, flocculating agents, drainage and/or retention assistants. The stock concentration may vary in any conventional range as suitable for the employed pulp, machine, process and desired paper quality, e.g. in the range of 0.4 to 10 %, preferably 0.8 to 6 %, by weight of dry pulp. According to a particular feature of the invention there is employed a pulp from coated broke optionally blended with other pulp.

The polycationic polymers (P) are preferably employed in a concentration in the range of 0.05 to 0.5 % by weight, more preferably 0.1 to 0.4 % by weight referred to dry pulp. There may be employed as (P) only one kind of (P) e.g. (P₁), (P_{2'}) or (P_{2''}) alone or also a mixture of two or more thereof, e.g. a mixture of (P₁) with (P_{2'}) or (P_{2''}) e.g. in the weight ratio of 10/90 to 90/10. The pH may be in the weakly basic to distinctly acidic range, preferably in the range of pH 4 to pH 8, more preferably pH 5 to pH 7. The paper may be produced using any conventional paper making machines and in a manner conventional per se. The resulting backwater is of reduced contaminants content, in particular of reduced turbidity, and consequently the respective BOD and/or COD values are also reduced. By the use of (P) there may also be achieved an improvement of the efficiency of other cationic wet-end additives such as flocculants, retention assistants or drainage assistants, and there may be obtained paper of optimum quality while paper breakings due to disturbing anionic contaminants is correspondingly reduced. The polycationic polymers (P) of the invention are also distinguished by their compatibility with optical brighteners as conventionally employed for paper.

In the following Examples parts and percentages are by weight, if not otherwise indicated; parts by weight relate to parts by volume as grams to milliliters. The temperatures are indicated in degrees Celsius.

Example 1

109.2 parts of sorbitol are mixed with 55.2 parts of glycerol and heated to 100°C to form a solution. One part of boron trifluoride etherate is added and the mixture is stirred and cooled to 70°C. 333 parts of epichlorohydrin are added dropwise over one hour at 70-80°C with cooling. The reaction mixture is cooled to 20°C and 135 parts of an aqueous 60 % dimethylamine solution are added and the reaction mixture is heated slowly to 90°C and held for one hour. The reaction mixture is then cooled to 50°C and 150 parts of 30 % sodium hydroxide and 100 parts of water are added. The mixture is held at 50 - 60°C and the mixture slowly thickens as it polymerises. During this time extra water is added (275 parts) as the viscosity increases. Finally when the reaction mixture reaches the viscosity of 1000 cP the reaction is stopped by the addition of 20 parts of formic acid to give a pH of 4.

Example 2

The procedure described in Example 1 is repeated, with the difference that 81.6 parts of pentaerythritol are used in place of 109.2 parts of sorbitol.

Example 3

The procedure described in Example 1 is repeated, with the difference that 37.2 parts of ethylene glycol are employed instead of 55.2 parts of glycerol.

Example 4

The procedure described in Example 1 is repeated, with the difference that 208.8 parts of tetramethylethylenediamine are employed instead of 135 parts of dimethylamine.

Example 5

The procedure described in Example 1 is repeated, with the difference that 110.4 parts of glycerol are employed instead of the mixture of 109.2 parts of sorbitol and 55.2 parts of glycerol.

Example 6

500 parts of polyethylene glycol 200 are heated to 70°C and 2 parts of boron trifluoride etherate are added. 693.75 parts of epichlorohydrin are added dropwise over two hours at 80-85°C with stirring. The reaction mixture is cooled to 50°C and 267.4 parts of N,N-dimethylaminopropylamine are added and the pH is adjusted at 8.5-9 by addition of a 30 % sodium hydroxide solution. The reaction mixture is kept at 50°C and pH 8.5 and diluted slowly with 3000 parts of water as the reaction mixture thickens. When the viscosity reaches 1000 cP at 50°C formic acid is added to the mixture until the pH is 4.

Example 7

The procedure described in Example 6 is repeated, with the difference that instead of polyethylene 200 there is employed the equivalent amount of polyethylene 400.

Example 8

The procedure described in Example 6 is repeated, with the difference that instead of dimethylaminopropylamine there is employed the equivalent amount of tetramethylethylenediamine.

Application Example A

100 ml of pulp are measured into a beaker and stirred at 500 rpm. The pulp is filtered through a Whatman No. 541 paper and the filtrates are retained. The COD of the filtrates is measured using standard procedures as set out by the spectrophotometer being used (Hach or Dr. Lange). Similarly the turbidity is measured using a spectrophotometer. The above procedure is repeated but this time the pulp is dosed with the cationic polymer of Example 1 at levels equivalent to 1, 2, 3 and 4 kg/t before filtration. The COD and turbidity of the filtrates are measured and compared with the blank test. There are obtained improved values.

Application Examples B, C, D, E, F and G

Application Example A is repeated, with the difference that instead of the cationic polymer of Example 1, there is employed the same amount amounts of those of Examples 2, 3, 4, 5, 6 and 7 respectively. There are obtained in each case improved values in comparison with the blank test.

CLAIMS

1. A polycationic polyquaternary product (P) obtainable by reaction of

- (A) an oligohydroxyalkane of molecular weight ≥ 92 , in which the the alkane backbone is optionally interrupted by one or more ether bridges,
or a mixture of two or more thereof,
or a mixture one or more thereof with a C₂₋₃-alkanediol,

with (B) epichlorohydrin,

in the ratio of at least 1 mole of epichlorohydrin for every moleequivalent of oligohydroxy-compound of molecular weight ≥ 92 plus 1-4 moles of epichlorohydrin for every moleequivalent of C₂₋₃-alkanediol,
to give a chloro-terminated adduct (E),

and quaternizing, optionally cross-linking, reaction of (E) with

- (C) at least one aliphatic mono or oligoamine containing on average not more than one nitrogen-bound hydrogen per nitrogen atom.

2. A polycationic polyquaternary product (P) according to Claim 1 in which (A) is selected from

- (A₁) an oligohydroxyalkane of the formula



in which

X signifies the x₁-valent radical of a C₃₋₆-alkane
and x₁ signifies a number from 3 to the number of carbon atoms in X,
or a mixture of oligohydroxyalkanes of formula (Ia),
or a mixture one or more oligohydroxyalkanes of formula (Ia) with a C₂₋₃-alkanediol,

and (A₂) a polyalkylene glycol of the average formula



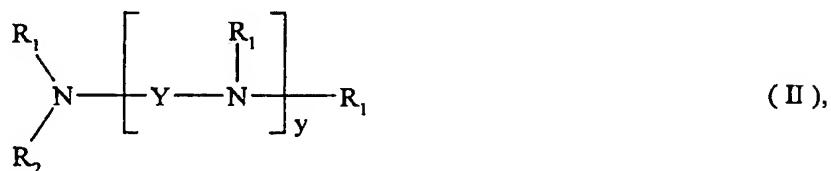
(Ib),

wherein

Alkylene signifies C₂₋₄-alkylene

and x2 signifies a number from 2 to 40.

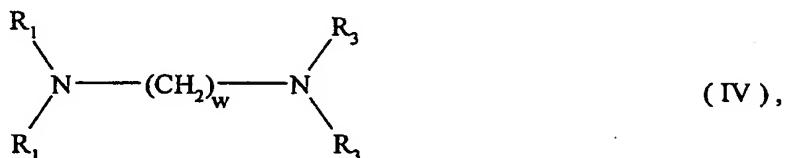
3. A polycationic polyquaternary product (P) according to Claim 1 or 2, in which (C) is selected from

(C₁) at least one aminocompound of formula

wherein

Y signifies C₂₋₃-alkylene,

y signifies a number from 0 to 3,

R₁ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyland R₂ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl, if y is 1 to 4,
or hydrogen, if y is 0,(C₂) a tertiary amine of formulaand (C₃) at least one diamine of formulawherein R₃ signifies hydrogen, C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl

and w signifies a number from 2 to 6.

4. A polycationic polyquaternary product (P) according to any one of Claims 1 to 3, which is a polycationic polymer (P_1) obtainable by reaction of

(A₁) an oligohydroxyalkane of the formula



in which

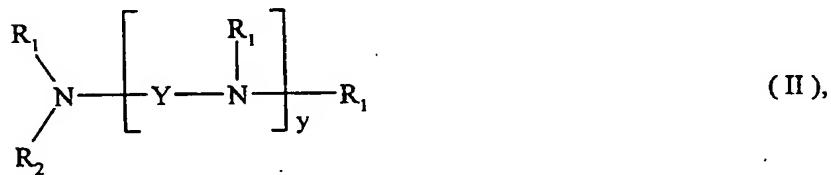
X signifies the x_1 -valent radical of a C₃₋₆-alkane
and x_1 signifies a number from 3 to the number of carbon atoms in X,
or a mixture of oligohydroxyalkanes of formula (Ia),
or a mixture one or more oligohydroxyalkanes of formula (Ia) with a C₂₋₃-alkanediol,

with (B) epichlorohydrin,

in the ratio of (2 to 2· x_1) moles of epichlorohydrin for every mole of oligohydroxy-C₃₋₆-alkane of formula (Ia) plus 1-4 moles of epichlorohydrin for every mole equivalent of C₂₋₃-alkanediol, to give a chloro-terminated adduct (E₁),

and reaction of (E₁) by cross-linking, quaternizing reaction with

(C₁) at least one aminocompound of formula



in which

Y signifies C₂₋₃-alkylene,
y signifies a number from 0 to 3,
R₁ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl,
and R₂ signifies C₁₋₃-alkyl or C₂₋₃-hydroxyalkyl, if y is 1 to 4,
or hydrogen, if y is 0,

and optionally chain-terminating, quaternizing reaction with

(C₂) a tertiary amine of formula

$N(R_1)_3$ (III).

5. A polycationic polyquaternary product (P) according to any one of Claims 1 to 3, which is a polycationic polymer (P₂) obtainable by reaction of

(A₂) an polyalkylene glycol of the average formula

$HO-(Alkylene-O)_{x2}-H$ (Ib),

wherein

Alkylene signifies C₂₋₄-alkylene

and x2 signifies a number from 2 to 40.

with (B) epichlorohydrin,

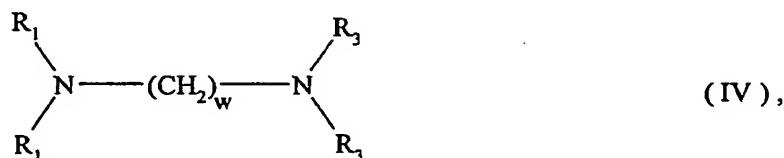
in the ratio of 2 or more moles of epichlorohydrin for every mole of polyalkylene glycol, to give a chloro-terminated adduct (E₂),

and reaction of (E₂) with

(C₂) a tertiary amine of formula

$N(R_1)_3$ (III)

or (C₃) at least one diamine of formula



wherein R₃ signifies hydrogen or C₁₋₃-alkyl
and w signifies a number from 2 to 6.

6. A polyquaternary polymer (P₁) according to Claim 4, wherein (A₁) is a mixture of glycerol and a compound of formula (Ia) in which x₁ is 4 to 6.
7. A polyquaternary product (P₂) according to Claim 5, wherein in (A₂) in formula (Ib) Alkylene is ethylene.
8. A polyquaternary product (P₂) according to Claim 5 or 7, wherein in (A₂) in formula (Ib) x₂ is a number in the range from 3 to 6 and quaternizing reaction is carried out with (C₂).
9. A polyquaternary product (P₂) according to Claim 5 or 7, wherein in (A₂) in formula (Ib) x₂ is a number in the range from 4 to 10 and quaternizing reaction is carried out with (C₃).
10. An aqueous composition comprising a polyquaternary product (P) according to any one of Claims 1 to 9.
11. Use of a polyquaternary product (P) according to any one of Claims 1 to 9, optionally in the form of an aqueous preparation according to Claim 10, as an adjuvant in papermaking.
12. Use of (P) according to Claim 11 as a fixative in the production of paper from coated broke.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/IB 99/01155

A. CLASSIFICATION OF SUBJECT MATTER

D21H17/52, C08G59/14

According to International Patent Classification (IPC) or to both national classification and IPC: 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H, C08G, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | DATABASE WPI, Week 8403, Derwent Publications Ltd., London, GB; Class D21H, AN 1984-015703; & SU 1002446 A (PAPER LENT. RES. INST.), 07 March 1983 abstract. -- WO 95/27008 A (HENKEL CORPORATION) 12 October 1995, claims. -- WO 95/15996 A (HENKEL CORPORATION) 15 June 1995, claims. ---- | 1, 2, 10-12 |
| A | | 1 |
| A | | 1 |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search
30 September 1999

Date of mailing of the international search report

25. 11. 1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 cpo nl.
Fax (+ 31-70) 340-3016

Authorized officer
PAMMINGER e.h.

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

à l'apport de recherche international relatif à la demande de brevet international n°

PCT/IB 99/01155 SAE 237889

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Orientierung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.

| Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche | Datum der Veröffentlichung Publication date Date de publication | Mitglied(er) der Patentfamilie Patent family members Membre(s) de la famille de brevets | Datum der Veröffentlichung Publication date Date de publication |
|---|---|---|---|
| SU A1 1002446 | 07-03-1983 | keine - none - rien | |
| WO A1 9527008 | 12-10-1995 | CA AA 2186622 EP A1 763073 EP A4 763073 JP T2 9511551 | 12-10-1995 19-03-1997 16-04-1997 18-11-1997 |
| WO A1 9515996 | 15-06-1995 | BR A 9408287 CA AA 2178616 EP A1 733086 EP A4 733086 US A 5492956 | 26-08-1997 15-06-1995 25-09-1995 10-09-1997 20-02-1996 |